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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/00755 A1

(54) Title: NATURAL GAS HYDRATE AND METHOD FOR PRODUCING SAME

(57) Abstract: A method for the production of the natural gas hydrate characterised by the steps of: combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system, allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature and reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

Natural Gas Hydrate And Method For Producing Same**Field Of The Invention**

The present invention relates to a natural gas hydrate. More particularly, the present invention relates to a natural gas hydrate with improved gas content and 5 stability characteristics and a method for producing the same.

**Background Art**

Natural gas hydrates are a stable solid comprising water and natural gas, and have been known to scientists for some years as a curiosity. More recently, natural gas hydrates became a serious concern in regard to the transportation 10 and storage of natural gas industries in cold climates, due to the tendency of hydrates to form in pipelines thereby blocking the flow the pipelines.

Natural gas hydrates may be formed by the combination of water and gas at relatively moderate temperatures and pressures, with the resulting solid having the outward characteristics of ice, being either white or grey in colour and cold to 15 the touch. At ambient temperatures and pressures natural gas hydrates break down releasing natural gas.

Conventionally, gas storage is achieved through re-injecting into reservoirs, or pressurised reservoirs or through the use of line pack, where the volume of the pipeline system is of the same order of magnitude as several days' customer 20 consumption. The use of natural gas hydrates in storage has the potential to provide a flexible way of storing reserves of natural gas to meet short to medium term requirements in the event of excessive demands or a reduction in the delivery of gas from source.

In any application, the gas content of the hydrate and the temperature at which 25 the hydrate begins to decompose (i.e. the hydrate desolution temperature), are significant criteria that require consideration. Known natural gas hydrates exhibit

a gas content of 163 Sm<sup>3</sup> per m<sup>3</sup> of hydrate, and a hydrate desolution temperature, at atmospheric pressure, of -15°C.

It is one object of the present invention to provide a natural gas hydrate and a method for the production thereof, with improved gas content and hydrate 5 desolution temperature.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

#### 10 Disclosure Of The Invention

In accordance with the present invention there is provided a natural gas hydrate with a gas content in excess of 163 Sm<sup>3</sup> per m<sup>3</sup>. Preferably, the natural gas hydrate has a gas content in excess of 170 Sm<sup>3</sup> per m<sup>3</sup>. Preferably still, the natural gas hydrate has a gas content in excess of 180 Sm<sup>3</sup> per m<sup>3</sup>. Further and 15 still preferably, the natural gas hydrate has a gas content of 186 Sm<sup>3</sup> per m<sup>3</sup>. In a highly preferred form of the invention, the natural gas hydrate has a gas content in excess of 220 Sm<sup>3</sup> per m<sup>3</sup>. Preferably still, the natural gas hydrate has a gas content in excess of approximately 227 Sm<sup>3</sup> per m<sup>3</sup>.

Preferably, the natural gas hydrate exhibits a hydrate desolution temperature in 20 excess of -15°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -13°C at atmospheric pressure. Further and still preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric pressure. In a highly preferred form of the invention, the natural gas hydrate exhibits a hydrate 25 desolution temperature in excess of -5°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of 3°C at atmospheric pressure.

In accordance with the present invention, there is further provided a natural gas hydrate which exhibits a hydrate desolution temperature in excess of -15°C at atmospheric pressure. Preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -13°C at atmospheric pressure. Preferably 5 still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric pressure. Further and still preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -5°C at atmospheric pressure. In a highly preferred form of the invention, the natural gas hydrate exhibits a hydrate desolution temperature in excess of 3°C at atmospheric 10 pressure.

Preferably, the natural gas hydrate has a gas content in excess of 163 Sm<sup>3</sup> per m<sup>3</sup>. Preferably still, the natural gas hydrate has a gas content in excess of 170 Sm<sup>3</sup> per m<sup>3</sup>. Further and still preferably, the natural gas hydrate has a gas content in excess of 180 Sm<sup>3</sup> per m<sup>3</sup>. In a highly preferred form of the invention, 15 the natural gas hydrate has a gas content of 186 Sm<sup>3</sup> per m<sup>3</sup>. In one form of the invention, the natural gas hydrate has a gas content in excess of 220 Sm<sup>3</sup> per m<sup>3</sup>. Preferably still, the natural gas hydrate has a gas content in excess of approximately 227 Sm<sup>3</sup> per m<sup>3</sup>.

In accordance with the present invention there is still further provided a method for 20 the production of the natural gas hydrate of the present invention, the method comprising the steps of:-

- 25 combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system;
- allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature; and
- reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

Preferably, the method of the present invention comprises the additional step of, before combining the natural gas and water, atomising the natural gas and water.

Preferably, the natural gas-water-agent system is agitated before the temperature is reduced.

5 Preferably, the agent is a compound that is at least partially soluble in water.

In one form of the invention, the agent is an alkali metal alkylsulfonate. Preferably, where the agent is an alkali metal alkylsulfonate, the alkali metal alkylsulfonate is a sodium alkylsulfonate. Where the agent is a sodium alkylsulfonate, the agent may be selected from the group; sodium lauryl sulfate, 10 sodium 1-propanesulfonate, sodium 1-butane sulfonate, sodium 1-pentanesulfonate, sodium 1-hexane sulfonate sodium 1-heptane sulfonate, sodium 1-octanesulfonate, sodium 1-nonanesulfonate, sodium 1-decanesulfonate, sodium 1-undecanesulfonate, sodium 1-dodecanesulfonate and sodium 1-tridecane sulfonate.

15 Where the agent is an alkali metal sulfonate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight. Preferably still, the amount of agent added results in a concentration of the agent less than about 0.5% by weight. Further and still preferably, the amount of agent added results in a concentration 20 of the agent between about 0.1 and 0.2% by weight.

In an alternate form of the invention, the agent is sodium lauryl sulfate. Where the agent is sodium lauryl sulfate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight. Preferably still, the amount of agent added results in a 25 concentration of the agent less than about 0.5% by weight. Further and still preferably, the amount of agent added results in a concentration of the agent between about 0.1 and 0.2% by weight.

In an alternate form of the invention, the agent is sodium tripolyphosphate. Where the agent is sodium tripolyphosphate, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is between about 1 and 3 % by weight.

- 5 In an alternate form of the invention, the agent is an alcohol. Preferably, where the agent is an alcohol, the agent is isopropyl alcohol. Where the agent is isopropyl alcohol, the amount of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is about 0.1 % by volume.
- 10 The degree to which the temperature is decreased depends upon the degree to which the pressure is elevated. However, preferably the pressure exceeds about 50 bars and preferably, the temperature is below about 18°C.

Preferably, the natural-gas-water-agent system is constantly mixed throughout the hydration process.

## 15 Examples

The present invention will now be described in relation to five examples. However, it must be appreciated that the following description of those examples is not to limit the generality of the above description of the invention.

### Hydrate Formation

#### 20 Example 1 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 25 a pressure of 206 bars (3000psia) and room temperature of 23°C.

- 6 -

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 17.7°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

5 Example 2 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 10 a pressure of 138 bars (2000psia) and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 15.5°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

15 Example 3 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at 20 a pressure of 102 bars and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 13.1°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

Example 4 – isopropyl alcohol

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly 5 by bubbling the methane through the water phase. The system was stabilised at a pressure of 54.5 bars (800psia) and room temperature of 23°C.

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 8.1°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when 10 pressure had stabilised in the cell.

Example 5 – sodium tripolyphosphate

Water and sodium tripolyphosphate (1% by weight) and methane gas were introduced into a sapphire cell. The pressure was adjusted to 1400 psia, and the mixture cooled rapidly to -5°C, where formation of the hydrate was observed. The 15 methane bubbling through the gas served to agitate the system.

Example 6 – sodium lauryl sulfate

Water and sodium lauryl sulfate (0.11% by weight) and methane gas were introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C, and left to equilibrate for 45 minutes. The mixture was then flashed into a 20 cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Example 7 – sodium 1-octanesulfonate

Water and sodium -octanesulfonate (0.15% by weight) and methane gas were introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C, 25 and left to equilibrate for 45 minutes. The mixture was then flashed into a

cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Example 8 – sodium 1-octanesulfonate

Water and sodium 1-octanesulfonate (0.1% by weight) and methane gas were 5 introduced into a sapphire cell. The mixture was pressurised to 2200psia at 30°C, and left to equilibrate for 45 minutes. The mixture was then flashed into a cryogenic PVT cell at -3°C, causing the fluid to atomise and resulting in the formation of hydrate.

Testing desolution temperature and natural gas content of hydrate

10 Example 1

Having formed the hydrate as outlined in Example 1, excess methane was removed and the temperature of the system was reduced to -15°C, at a rate of 0.1°C per minute, and the pressure of the system was observed to diminish to zero.

15 The hydrate was stored for more than 12 hours at -15°C, showing no observable changes in appearance. The pressure remained at zero throughout.

After 12 hours, the temperature of the system was gradually increased at a rate of 0.2°C per minute, in an attempt to reverse the hydrate formation process. Throughout this stage the pressure of the system was carefully monitored and 20 recorded by way of high precision digital pressure gauges. The pressure of the system remained stable until the temperature reached -11.5°C, at which point some increase was noted. The pressure continued to increase as the temperature increased until the pressure of the system stabilised at 206.3 bars at the ambient temperature of 23°C.

Quantities of methane and water generated from the desolution of the hydrate were measured, and the methane content of the methane hydrate was calculated to be 186 Sm<sup>3</sup> per m<sup>3</sup>.

Example 5

- 5 Having formed the hydrate as outlined in Example 5, the system was heated carefully. The hydrate was observed to melt at approximately 2°C. Based on the pressure-volume relationship, and excess methane before and after hydrate formation, the amount of methane contained in the hydrate was estimated to be in excess of 230 Sm<sup>3</sup> per m<sup>3</sup> of hydrate.

10 Examples 6 to 8

Having formed the hydrates as outlined in Examples 6 to 8, the systems were heated carefully. Each of the hydrates was observed to melt at approximately 3°C. Based on the pressure-volume relationship, and excess methane before and after hydrate formation, the amount of methane contained in the hydrate produced

- 15 in Example 6 was estimated to be in excess of 227 Sm<sup>3</sup> per m<sup>3</sup> of hydrate. Similarly, the amount of methane contained in the hydrate produced in Example 7 was estimated to be in excess of 212 Sm<sup>3</sup> per m<sup>3</sup> of hydrate. The amount of methane contained in the hydrate produced in Example 8 was estimated to be in excess of 209 Sm<sup>3</sup> per m<sup>3</sup> of hydrate.
- 20 Each unique mixture of hydrocarbon and water has its own hydrate formation curve, describing the temperatures and pressures at which the hydrate will form, and it is envisaged that additional analysis will reveal optimum pressure and temperature combinations, having regard to minimising the energy requirements for compression and cooling.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A natural gas hydrate characterised by a gas content in excess of 163 Sm<sup>3</sup> per m<sup>3</sup>.
2. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 170 Sm<sup>3</sup> per m<sup>3</sup>.  
5
3. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 180 Sm<sup>3</sup> per m<sup>3</sup>.
4. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 186 Sm<sup>3</sup> per m<sup>3</sup>.
- 10 5. A natural gas hydrate according to claim 1 characterised by a gas content in excess of 220 Sm<sup>3</sup> per m<sup>3</sup>.
6. A natural gas hydrate according to claim 1 characterised by a gas content in excess of approximately 227 Sm<sup>3</sup> per m<sup>3</sup>.
7. A natural gas hydrate according to any one of claims 1 to 6 characterised by a  
15 hydrate desolution temperature in excess of -15°C at atmospheric pressure.
8. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -13°C at atmospheric pressure.
9. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -11°C at atmospheric pressure.
- 20 10. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -5°C at atmospheric pressure.
11. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of -3°C at atmospheric pressure.

12. A natural gas hydrate according to claim 7 characterised by a hydrate desolution temperature in excess of 3°C at atmospheric pressure.
13. A method for the production of the natural gas hydrate of any one of claims 1 to 12 characterised by the steps of:-
  - 5        combining natural gas and water to form a natural-gas water system and an agent adapted to reduce the natural gas-water interfacial tension to form a natural-gas water-agent system;
  - allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature; and
  - 10      reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.
14. A method of according to claim 13 characterised by the additional step of, before combining the natural gas and water, atomising the natural gas and water.
15. A method according to claim 13 or claim 14 characterised by the natural gas-water-agent system being agitated before the temperature is reduced.
16. A method according to any one of claims 13 to 15 characterised in that the agent is a compound that is at least partially soluble in water.
17. A method according claim 16 characterised in that the agent is an alkali metal alkylsulfonate.
- 20      18. A method according to claim 17 characterised in that the alkali metal alkylsulfonate is a sodium alkylsulfonate.
- 25      19. A method according to claim 18 characterised in that the agent is selected from the group; sodium lauryl sulfate, sodium 1-propanesulfonate, sodium 1-butane sulfonate, sodium 1-pentanesulfonate, sodium 1-hexane sulfonate

sodium 1-heptane sulfonate, sodium 1-octanesulfonate, sodium 1-nonanesulfonate, sodium 1-decanesulfonate, sodium 1-undecanesulfonate, sodium 1-dodecanesulfonate and sodium 1-tridecane sulfonate.

20. A method according to any one of claims 17 to 19 characterised in that the  
5 amount of agent added is such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.
21. A method according to claim 20 characterised in that the amount of agent added results in a concentration of the agent less than about 0.5% by weight.
22. A method according to claim 21 characterised in that the amount of agent  
10 added results in a concentration of the agent between about 0.1 and 0.2% by weight.
23. A method according to claim 16 characterised in that the agent is sodium lauryl sulfate.
24. A method according to claim 23 characterised in that the amount of agent  
15 added is preferably such that the concentration of the agent in the natural gas-water-agent system is less than about 1% by weight.
25. A method according to claim 24 characterised in that the amount of agent added results in a concentration of the agent less than about 0.5% by weight.
26. A method according to claim 25 characterised in that the amount of agent  
20 added results in a concentration of the agent between about 0.1 and 0.2% by weight.
27. A method according to claim 16 characterised in that the agent is sodium tripolyphosphate.
28. A method according to claim 27 characterised in that the amount of agent  
25 added is preferably such that the concentration of the agent in the natural gas-water-agent system is between about 1 and 3 % by weight.

29. A method according to claim 16 characterised in that the agent is an alcohol.
30. A method according to claim 29 characterised in that the agent is isopropyl alcohol.
31. A method according to either claim 29 or 30 characterised in that the amount  
5 of agent added is preferably such that the concentration of the agent in the natural gas-water-agent system is about 0.1 % by volume.
32. A method according to any one of claims 13 to 31 characterised in that the pressure exceeds about 50 bars.
33. A method according to any one of claims 13 to 32 characterised in that the  
10 temperature is below about 18°C.
34. A method according to any one of the preceding claims wherein the natural-gas-water-agent system is constantly mixed throughout the method.
35. A method for the production of the natural gas hydrate substantially described herein with reference to any one of Examples 1 to 8.
- 15 36. A natural gas hydrate substantially as herein described.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU00/00719

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. 7: C10L 3/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C10L 3/10, 3/06, 3/00Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
AU:IPC as aboveElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
WPAT:(HYDRATE+ or CLATHRAT+) and (SULPHONAT+ OR SULFONAT+ OR SULPHAT+ OR SULFAT+)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No.           |
|-----------|--|---------------------------------|
| X         | US 5 536 893 A (Gudmundsson) 16 July 1996<br>See column(s) 2 lines 22-63, 5 lines 9-35, 7 lines 14-27, 9 lines 61-67 and Figure 1.                 | 1-2, 7-19, 23, 27, 29-30, 32-34 |
| X         | WO 93 01153 A (Gudmundsson) 21 January 1993<br>See page(s) 2 lines 18-19, 7 lines 5-7, 9 lines 11-23, 10 lines 14-21, 14 lines 12-16 and Figure 1. | 1-2, 7-19, 23, 27, 29-30, 32-34 |
| X         | WO 99 19662 A (MOBIL OIL CORPORATION) 22 April 1999<br>See page 1 lines 8-23.  | 1-2                             |

Further documents are listed in the continuation of Box C  See patent family annex

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| * Special categories of cited documents:  |  |
| "A" document defining the general state of the art which is not considered to be of particular relevance  | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
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| Date of the actual completion of the international search<br>15 August 2000 | Date of mailing of the international search report<br>25 AUG 2000 |
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| Name and mailing address of the ISA/AU<br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaustralia.gov.au<br>Facsimile No. (02) 6285 3929 | Authorized officer<br>JOHN DEUIS<br>Telephone No : (02) 6283 2146 |
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU00/00719

## C (Continuation).

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | US 3 975 167 A (Nierman) 17 August 1976  |                       |
| A         | GB 2 309 227 A (British Gas plc) 23 July 1997                                      |                       |

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/AU00/00719**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report |         |      | Patent Family Member |    |         |    |          |
|--|---------|------|----------------------|----|---------|----|----------|
| US                                     | 5536893 | NONE |                      |    |         |    |          |
| WO                                     | 9301153 | EP   | 594616               | NO | 900395  | NO | 9000395  |
| WO                                     | 9919662 | AU   | 95825/98             | EP | 1025385 | NO | 20001861 |
|  |         | US   | 5964093              |    |         |    |          |
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|  |         | DK   | 1386/76              | GB | 1534768 | GB | 1534769  |
|  |         | NO   | 761027               |    |         |    |          |
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|  |         | DK   | 1007/97              | EP | 820574  | NZ | 325367   |
|  |         | PL   | 322305               | WO | 9726494 |    |          |
| END OF ANNEX                           |         |      |                      |    |         |    |          |

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